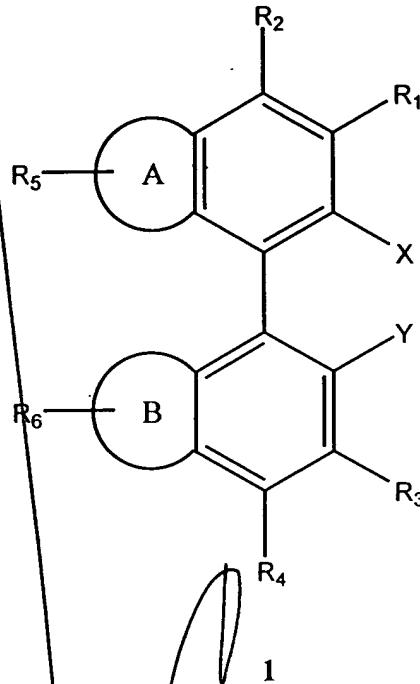


We claim:

1. The ligand represented by general structure 1:



wherein

5 each of A and B independently represent fused rings selected from a group consisting of monocyclic or polycyclic cycloalkyls, cycloalkenyls, aryls, and heterocyclic rings, said rings comprising from 4 to 8 atoms in a ring structure;

X and Y represent, independently for each occurrence, NR_2 , PR_2 , AsR_2 , OR , or SR ;

10 R, R_1 , R_2 , R_3 , and R_4 , for each occurrence, independently represent hydrogen, halogen, alkyl, alkenyl, alkynyl, hydroxyl, alkoxy, silyloxy, amino, nitro, sulfhydryl, alkylthio, imine, amide, phosphoryl, phosphonate, phosphine, carbonyl, carboxyl, carboxamide, anhydride, silyl, thioalkyl, alkylsulfonyl, arylsulfonyl, selenoalkyl, ketone, aldehyde, ester, heteroalkyl, nitrile, guanidine, amidine, acetal, ketal, amine oxide, aryl, heteroaryl, azide, aziridine, carbamate, epoxide, hydroxamic acid, imide, oxime, sulfonamide, thioamide, thiocarbamate, urea, thiourea, 15 or $-(CH_2)_m-R_{80}$;

R₅ and R₆, for each occurrence, independently represent halogen, alkyl, alkenyl, alkynyl, hydroxyl, alkoxy, silyloxy, amino, nitro, sulfhydryl, alkylthio, imine, amide, phosphoryl, phosphonate, phosphine, carbonyl, carboxyl, carboxamide, anhydride, silyl, thioalkyl, alkylsulfonyl, arylsulfonyl, selenoalkyl, ketone, aldehyde, ester, heteroalkyl, nitrile, guanidine, 5 amidine, acetal, ketal, amine oxide, aryl, heteroaryl, azide, aziridine, carbamate, epoxide, hydroxamic acid, imide, oxime, sulfonamide, thioamide, thiocarbamate, urea, thiourea, or -(CH₂)_m-R₈₀;

A and B independently may be unsubstituted or substituted with R₅ and R₆, respectively, any number of times up to the limitations imposed by stability and the rules of 10 valence;

R₁ and R₂, and/or R₃ and R₄, taken together may represent a ring comprising a total of 5-7 atoms in the backbone of said ring; said ring may comprise one or two heteroatoms in its backbone; and said ring may bear additional substituents or be unsubstituted;

15 R₈₀ represents an unsubstituted or substituted aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle;

m is an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, may be provided in the form of a mixture of enantiomers or as a single enantiomer.

20 2. The ligand of claim 1, wherein

X and Y are not identical;

R is selected, independently for each occurrence, from the set consisting of alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, and -(CH₂)_m-R₈₀;

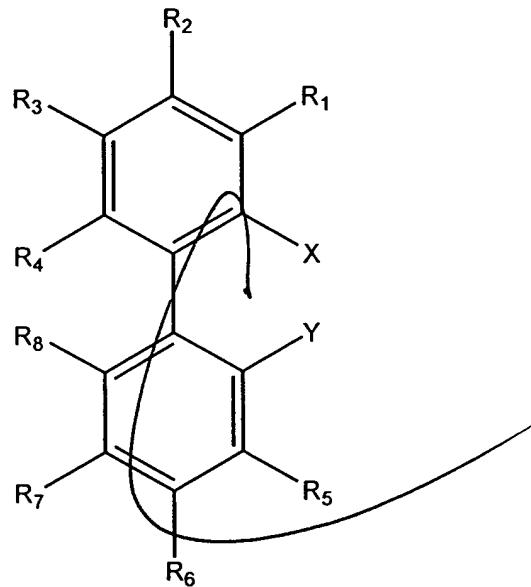
25 R₁, R₂, R₃, and R₄ are selected, independently for each occurrence, from the set consisting of H, alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, halogen, -SiR₃, and -(CH₂)_m-R₈₀; and

R_5 and R_6 are selected, independently for each occurrence, from the set consisting of H, alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, halogen, $-\text{SiR}_3$, and $-(\text{CH}_2)_m-\text{R}_{80}$.

5 3. The ligand of claim 1, wherein X is hydrogen; and Y is PR_2 .

4. The ligand of claim 3, wherein R is alkyl.

5. The ligand represented by general structure 2:



10 wherein

X and Y represent, independently for each occurrence, NR_2 , PR_2 , AsR_2 , OR, or SR;

15 R, R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , and R_8 , for each occurrence, independently represent hydrogen, halogen, alkyl, alkenyl, alkynyl, hydroxyl, alkoxy, silyloxy, amino, nitro, sulphydryl, alkylthio, imine, amide, phosphoryl, phosphonate, phosphine, carbonyl, carboxyl, carboxamide, anhydride, silyl, thioalkyl, alkylsulfonyl, arylsulfonyl, selenoalkyl, ketone, aldehyde, ester,

heteroalkyl, nitrile, guanidine, amidine, acetal, ketal, amine oxide, aryl, heteroaryl, azide, aziridine, carbamate, epoxide, hydroxamic acid, imide, oxime, sulfonamide, thioamide, thiocarbamate, urea, thiourea, or $-(CH_2)_m-R_{80}$;

any pair(s) of substituents, with an *ortho*-relationship therebetween, selected from the
5 group consisting of R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , and R_8 , taken together may represent a ring comprising a total of 5-7 atoms in the backbone of said ring; said ring may comprise one or two heteroatoms in its backbone; and said ring may bear additional substituents or be unsubstituted;

R_{80} represents an unsubstituted or substituted aryl, a cycloalkyl, a cycloalkenyl, a
10 heterocycle, or a polycycle;

m is an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, may be provided in the form of a mixture of enantiomers or as a single enantiomer.

15 6. The ligand of claim 5, wherein:

X and Y are not identical;

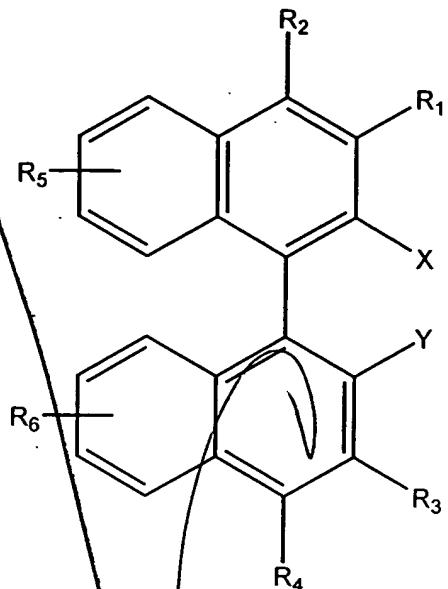
R is selected, independently for each occurrence, from the set consisting of alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, and $-(CH_2)_m-R_{80}$;

20 R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , and R_8 are selected, independently for each occurrence, from the set consisting of H, alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, halogen, $-SiR_3$, and $-(CH_2)_m-R_{80}$.

7. The ligand of claim 5, wherein X is hydrogen; and Y is PR_2 .

25 8. The ligand of claim 7, wherein R is alkyl.

9. The ligand represented by general structure 3:



wherein

X and Y represent, independently for each occurrence, NR₂, PR₂, AsR₂, OR, or SR;

R, R₁, R₂, R₃, and R₄, for each occurrence, independently represent hydrogen, halogen, 5 alkyl, alkenyl, alkynyl, hydroxyl, alkoxy, silyloxy, amino, nitro, sulphydryl, alkylthio, imine, amide, phosphoryl, phosphonate, phosphine, carbonyl, carboxyl, carboxamide, anhydride, silyl, thioalkyl, alkylsulfonyl, arylsulfonyl, selenoalkyl, ketone, aldehyde, ester, heteroalkyl, nitrile, guanidine, amidine, acetal, ketal, amine oxide, aryl, heteroaryl, azide, aziridine, carbamate, epoxide, hydroxamic acid, imide, oxime, sulfonamide, thioamide, thiocarbamate, urea, thiourea, 10 or -(CH₂)_m-R₈₀;

R₅ and R₆, for each occurrence, independently represent halogen, alkyl, alkenyl, alkynyl, hydroxyl, alkoxy, silyloxy, amino, nitro, sulphydryl, alkylthio, imine, amide, phosphoryl, phosphonate, phosphine, carbonyl, carboxyl, carboxamide, anhydride, silyl, thioalkyl, alkylsulfonyl, arylsulfonyl, selenoalkyl, ketone, aldehyde, ester, heteroalkyl, nitrile, guanidine, amidine, acetal, ketal, amine oxide, aryl, heteroaryl, azide, aziridine, carbamate, epoxide, hydroxamic acid, imide, oxime, sulfonamide, thioamide, thiocarbamate, urea, thiourea, 15 or -(CH₂)_m-R₈₀;

the B and B' rings of the binaphthyl core independently may be unsubstituted or substituted with R₅ and R₆, respectively, any number of times up to the limitations imposed by stability and the rules of valence;

5 R₁ and R₂, and/or R₃ and R₄, taken together may represent a ring consisting of a total of 5-7 atoms in the backbone of said ring; said ring may comprise one or two heteroatoms in its backbone; and said ring may bear additional substituents or be unsubstituted;

R₈₀ represents an unsubstituted or substituted aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle;

m is an integer in the range 0 to 8 inclusive; and

10 the ligand, when chiral, may be provided in the form of a mixture of enantiomers or as a single enantiomer.

10. The ligand of claim 9, wherein:

X and Y are not identical;

15 R is selected, independently for each occurrence, from the set consisting of alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, and -(CH₂)_m-R₈₀:

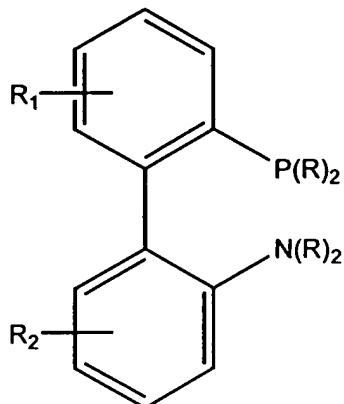
R₁, R₂, R₃, and R₄ are selected, independently for each occurrence, from the set consisting of H, alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, halogen, -SiR₃, and -(CH₂)_m-R₈₀; and

R₅ and R₆ are selected, independently for each occurrence, from the set consisting of alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, halogen, -SiR₃, and -(CH₂)_m-R₈₀.

11. The ligand of claim 9, wherein X is hydrogen; and Y is PR₂.

25 12. The ligand of claim 11, wherein R is alkyl.

13. The ligand represented by general structure 4:



wherein

R is selected, independently for each occurrence, from the set consisting of alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, and $-(CH_2)_m-$

5 R_{80} ;

the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R_1 and R_2 , respectively, any number of times up to the limitations imposed by stability and the rules of valence;

10 R_1 and R_2 are selected, independently for each occurrence, from the set consisting of alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, halogen, $-SiR_3$, and $-(CH_2)_m-R_{80}$;

R_{80} represents an unsubstituted or substituted aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle;

m is an integer in the range 0 to 8 inclusive; and

15 the ligand, when chiral, may be provided in the form of a mixture of enantiomers or as a single enantiomer.

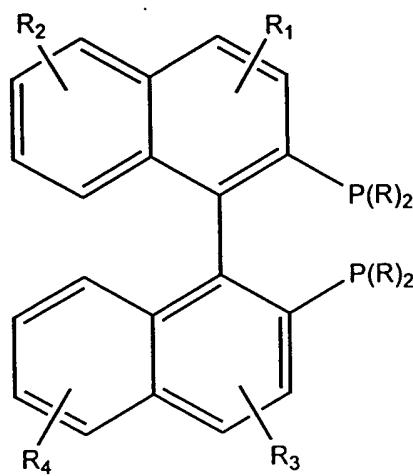
14. The ligand of claim 13, wherein:

R_1 and R_2 are absent;

both instances of R on the N depicted explicitly are lower alkyl; and

both instances of R on P depicted explicitly are cycloalkyl.

15. The ligand represented by general structure 5:



5

wherein

R is selected, independently for each occurrence, from the set consisting of alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, and -(CH₂)_m-R₈₀;

10 the A, B, A', and B' rings of the binaphthyl core independently may be unsubstituted or substituted with R₁, R₂, R₃, and R₄, respectively, any number of times up to the limitations imposed by stability and the rules of valence;

15 R₁, R₂, R₃, and R₄, are selected, independently for each occurrence, from the set consisting of alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, halogen, -SiR₃, and -(CH₂)_m-R₈₀;

R₈₀ represents an unsubstituted or substituted aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle;

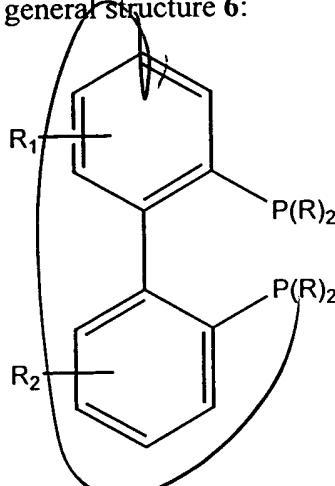
m is an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, may be provided in the form of a mixture of enantiomers or as a single enantiomer.

16. The ligand of claim 15, wherein:

5 R_1 , R_2 , R_3 , and R_4 , are absent; and
all instances of R are lower alkyl or cycloalkyl.

17. The ligand represented by general structure 6:



10 wherein

R is selected, independently for each occurrence, from the set consisting of alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, and $-(CH_2)_m-R_{80}$;

15 the A and A' rings of the biphenyl core independently may be unsubstituted or substituted with R_1 and R_2 , respectively, any number of times up to the limitations imposed by stability and the rules of valence;

R_1 and R_2 are selected, independently for each occurrence, from the set consisting of alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl,

halogen, $-\text{SiR}_3$, and $-(\text{CH}_2)_m-\text{R}_{80}$;

R_{80} represents an unsubstituted or substituted aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle;

m is an integer in the range 0 to 8 inclusive; and

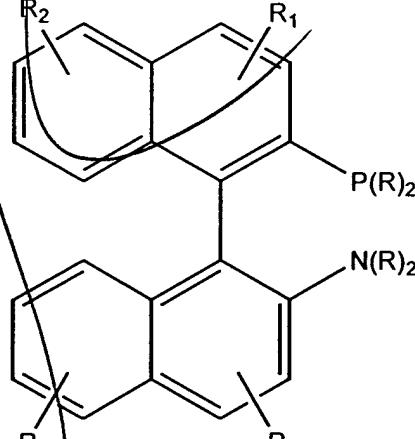
5 the ligand, when chiral, may be provided in the form of a mixture of enantiomers or as a single enantiomer.

18. The ligand of claim 17, wherein:

10 R_1 and R_2 are absent; and

all instances of R are lower alkyl or cycloalkyl.

19. The ligand represented by general structure 7:



wherein

15 R is selected, independently for each occurrence, from the set consisting of alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, and $-(\text{CH}_2)_m-\text{R}_{80}$;

the A, B, A', and B' rings of the binaphthyl core independently may be unsubstituted or substituted with R₁, R₂, R₃, and R₄, respectively, any number of times up to the limitations imposed by stability and the rules of valence;

5 R₁, R₂, R₃, and R₄, are selected, independently for each occurrence, from the set consisting of alkyl, heteroalkyl, cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl, heteroaralkyl, halogen, -SiR₃, and -(CH₂)_m-R₈₀;

R₈₀ represents an unsubstituted or substituted aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle;

10 m is an integer in the range 0 to 8 inclusive; and

the ligand, when chiral, may be provided in the form of a mixture of enantiomers or as a single enantiomer.

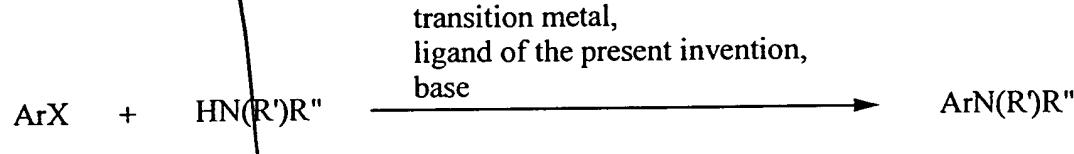
20. The ligand of claim 19, wherein:

R₁, R₂, R₃, and R₄, are absent;

15 both instances of R on the N depicted explicitly are lower alkyl; and

both instances of R on P depicted explicitly are cycloalkyl.

21. The method depicted in Scheme 1:



Scheme 1

20 wherein

Ar is selected from the set consisting of optionally substituted monocyclic and polycyclic aromatic and heteroaromatic moieties;

X is selected from the set consisting of Cl, Br, I, -OS(O)₂alkyl, and -OS(O)₂aryl;

*Sub
cl*

R' and R" are selected, independently for each occurrence, from the set consisting of H, alkyl, heteroalkyl, aryl, heteroaryl, aralkyl, alkoxy, amino, trialkylsilyl, and triarylsilyl;

R' and R", taken together, may form an optionally substituted ring consisting of 3-10 backbone atoms inclusive; said ring optionally comprising one or more heteroatoms beyond the nitrogen to which R' and R" are bonded;

R' and/or R" may be covalently linked to Ar such that the amination reaction is intramolecular;

the transition metal is selected from the set consisting of the Group VIIIA metals;

the ligand is selected from the set consisting of 1-7 inclusive; and

the base is selected from the set consisting of hydrides, carbonates, phosphates, alkoxides, amides, carbanions, and silyl anions.

22. The method of claim 21, wherein:

the ligand is 2;

15 the transition metal is palladium; and

the base is an alkoxide, amide, phosphate, or carbonate.

23. The method of claim 21 or 22, wherein:

the ligand is 2, wherein X is hydrogen, and Y represents P(alkyl)₂; and

20 X represents Cl or Br.

24. The method of claim 21, wherein:

the ligand is 4;

the transition metal is palladium; and

25 the base is an alkoxide, amide, phosphate, or carbonate.

Sub C1

25. The method of claim 22, wherein:

the ligand is 4, wherein R_1 and R_2 are absent; $P(R)_2$ represents PCy_2 , and $N(R)_2$ represents NMe_2 ; and

5 X represents Cl or Br.

Sub C2

26. The method of claim 21, wherein: $HN(R')R''$ represents an optionally substituted heteroaromatic compound.

10 27. The method of claim 21, wherein: X represents Cl; the ligand is 4, wherein R_1 and R_2 are absent, $P(R)_2$ represents PCy_2 , and $N(R)_2$ represents NMe_2 ; the transition metal is palladium; and the base is an alkoxide, amide, phosphate, or carbonate.

15 28. The method of claim 21, wherein: X represents Br or I; the ligand is 4, wherein R_1 and R_2 are absent, $P(R)_2$ represents PCy_2 , and $N(R)_2$ represents NMe_2 ; the transition metal is palladium; the base is an alkoxide, amide, phosphate, or carbonate; and the transformation occurs at room temperature.

20 29. The method of claim 21, wherein: the ligand is 5; the transition metal is palladium; and the base is an alkoxide, amide, phosphate, or carbonate.

30. The method of claim 21, wherein: X represents Cl; the ligand is 5, wherein R_1 , R_2 , R_3 , and R_4 are absent, and all occurrences of R are cyclohexyl; the transition metal is palladium; and the base is an alkoxide, amide, phosphate, or carbonate.

25 32. The method of claim 21, wherein: the ligand is 2, wherein X and Y both represent P; the transition metal is palladium; and the base is an alkoxide, amide, phosphate, or carbonate.

Sub C3

5
SUB C3
33. The method of claim 21, wherein: X represents Cl; the ligand is 2, wherein X and Y both represent P, R₁, R₂, R₃, R₄, R₅, R₆, R₇, and R₈ are absent, and all occurrences of R are cyclohexyl; the transition metal is palladium; and the base is an alkoxide, amide, phosphate, or carbonate.

34. The method of claim 21, wherein (alkenyl)X serves as a surrogate for ArX.

10 35. The method of claim 21, wherein the product is provided in a yield of greater than 50%.

36. The method of claim 21, wherein the product is provided in a yield of greater than 70%.

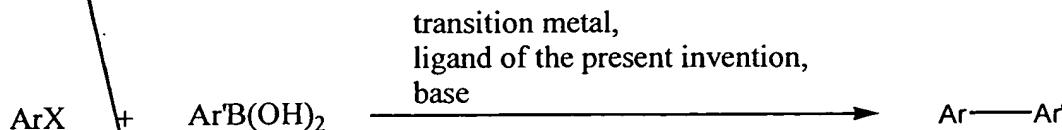
37. The method of claim 21, wherein the product is provided in a yield of greater than 85%.

38. The method of claim 21, wherein the reaction occurs at ambient temperature.

15 39. The method of claim 21, wherein the catalyst complex is present in less than 0.01 mol% relative to the limiting reagent.

40. The method of claim 21, wherein the catalyst complex is present in less than 0.0001 mol% relative to the limiting reagent.

41. The method depicted in Scheme 2:



Scheme 2

wherein

Ar and Ar' are independently selected from the set consisting of optionally substituted monocyclic and polycyclic aromatic and heteroaromatic moieties;

Sub C4

X is selected from the set consisting of Cl, Br, I, -OS(O)₂alkyl, and -OS(O)₂aryl; Ar and Ar' may be covalently linked such that the reaction is intramolecular; the transition metal is selected from the set consisting of the Group VIIIA metals; the ligand is selected from the set consisting of 1-7 inclusive; and

5 the base is selected from the set consisting of carbonates, phosphates, fluorides, alkoxides, amides, carbanions, and silyl anions.

42. The method of claim 41, wherein

the ligand is 2;

10 the transition metal is palladium; and

the base is an alkoxide, amide, phosphate, or carbonate.

43. The method of claim 41 or 42, wherein

the ligand is 2, wherein X is hydrogen, and Y represents P(alkyl)₂; and

15 X represents Cl or Br.

44. The method of claim 41, wherein:

the transition metal is palladium;

the ligand is 4; and

20 the base is an alkoxide, amide, carbonate, phosphate, or fluoride.

45. The method of claim 41, wherein:

the ligand is 4, wherein R₁ and R₂ are absent; P(R)₂ represents PCy₂, and N(R)₂ represents NMe₂;

25 X represents Cl or Br; and

*Sub
Ch*

the reaction occurs at room temperature.

46. The method of claim 41, wherein (alkenyl)X serves as a surrogate for ArX, and/or (alkenyl)B(OH)₂ serves as a surrogate for ArB(OH)₂.

5

47. The method of claim 41, wherein the product is provided in a yield of greater than 50%.

48. The method of claim 41, wherein the product is provided in a yield of greater than 70%.

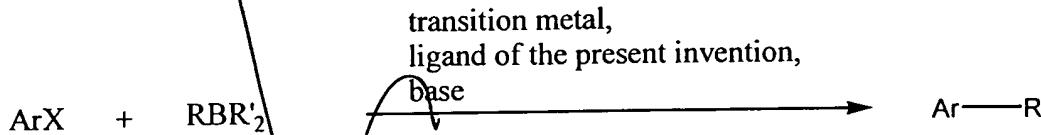
10 49. The method of claim 41, wherein the product is provided in a yield of greater than 85%.

50. The method of claim 41, wherein the reaction occurs at ambient temperature.

51. The method of claim 41, wherein the catalyst complex is present in less than 0.01 mol% relative to the limiting reagent.

15 52. The method of claim 41, wherein the catalyst complex is present in less than 0.0001 mol% relative to the limiting reagent.

53. The method depicted in Scheme 3:



Scheme 3

20 wherein

Ar is selected from the set consisting of optionally substituted monocyclic and polycyclic aromatic and heteroaromatic moieties;

R is selected from the set consisting of optionally substituted alkyl, heteroalkyl, and aralkyl;

R' is selected, independently for each occurrence, from the set of alkyl and heteroalkyl; the carbon-boron bond of said alkyl and heteroalkyl groups being inert under the reaction conditions, e.g., BR_2 , taken together represents 9-borabicyclo[3.3.1]nonyl.

X is selected from the set consisting of Cl, Br, I, -OS(O)₂alkyl, and -OS(O)₂aryl;

Ar and R may be covalently linked such that the reaction is intramolecular;

the transition metal is selected from the set consisting of the Group VIIIA metals;

the ligand is selected from the set consisting of 1-7 inclusive; and

10 the base is selected from the set consisting of carbonates, phosphates, fluorides, alkoxides, amides, carbanions, and silyl anions.

54. The method of claim 53, wherein:

the ligand is 2;

the transition metal is palladium; and

15 the base is an alkoxide, amide, phosphate, or carbonate.

55. The method of claim 53 or 54, wherein:

the ligand is 2, wherein X is hydrogen, and Y represents P(alkyl)₂; and

X represents Cl or Br.

20

56. The method of claim 53, wherein

X represents Cl or Br;

the transition metal is palladium;

the ligand is 4; and

25 the base is an alkoxide, amide, carbonate, phosphate, or fluoride.

57. The method of claim 53, wherein

the ligand is 4, wherein R_1 and R_2 are absent; $P(R)_2$ represents PCy_2 , and $N(R)_2$ represents NMe_2 ; and

5 X represents Cl.

58. The method of claim 53, wherein (alkenyl)X serves as a surrogate for ArX.

59. The method of claim 53, wherein the product is provided in a yield of greater than

10 50%.

60. The method of claim 53, wherein the product is provided in a yield of greater than 70%.

61. The method of claim 53, wherein the product is provided in a yield of greater than 85%.

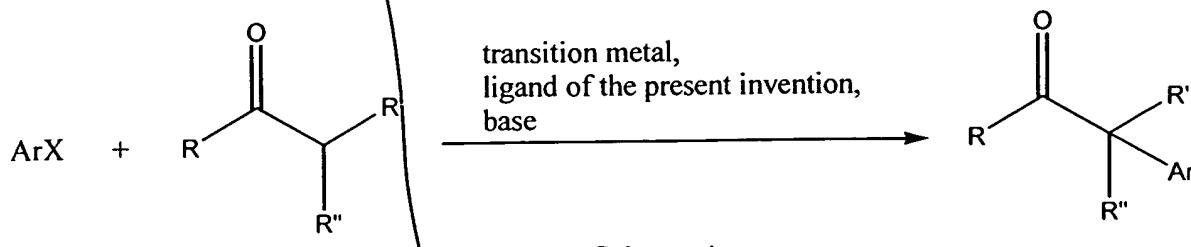
15 62. The method of claim 53, wherein the reaction occurs at ambient temperature.

63. The method of claim 53, wherein the catalyst complex is present in less than 0.01 mol% relative to the limiting reagent.

64. The method of claim 53, wherein the catalyst complex is present in less than 0.0001 mol% relative to the limiting reagent.

20

65. The method depicted in Scheme 4:



Scheme 4

wherein

Ar is selected from the set consisting of optionally substituted monocyclic and polycyclic aromatic and heteroaromatic moieties;

5 R, R', and R" are selected, independently for each occurrence, from the set consisting of H, alkyl, heteroalkyl, aralkyl, aryl, heteroaryl;

X is selected from the set consisting of Cl, Br, I, -OS(O)₂alkyl, and -OS(O)₂aryl;

Ar and one of R, R', and R" may be covalently linked such that the reaction is intramolecular;

10 the transition metal is selected from the set consisting of the Group VIIIA metals;

the ligand is selected from the set consisting of 1-7 inclusive; and

the base is selected from the set consisting of carbonates, phosphates, fluorides, alkoxides, amides, carbanions, and silyl anions.

66. The method of claim 65, wherein

15 the ligand is 2;

the transition metal is palladium; and

the base is an alkoxide, amide, phosphate, or carbonate.

67. The method of claim 65 or 66, wherein

20 the ligand is 2, wherein X is hydrogen, and Y represents P(alkyl)₂; and

X represents Cl or Br.

68. The method of claim 65, wherein

25 X represents Cl or Br;

the transition metal is palladium;

the ligand is 4; and
the base is an alkoxide, or amide.

69. The method of claim 65, wherein
5 the ligand is 4, wherein R₁ and R₂ are absent; P(R)₂ represents PCy₂, and N(R)₂ represents NMe₂.

70. The method of claim 65, wherein
10 X represents Br; and
the reaction occurs at room temperature.

71. The method of claim 65, wherein (alkenyl)X serves as a surrogate for ArX.

72. The method of claim 65, wherein the product is provided in a yield of greater than
15 50%.

73. The method of claim 65, wherein the product is provided in a yield of greater than
70%.

74. The method of claim 65, wherein the product is provided in a yield of greater than 85%.

75. The method of claim 65, wherein the reaction occurs at ambient temperature.

20 76. The method of claim 65, wherein the catalyst complex is present in less than 0.01 mol% relative to the limiting reagent.

77. The method of claim 65, wherein the catalyst complex is present in less than 0.0001 mol% relative to the limiting reagent.

25 78. The method of claim 21, 41, 53, or 65, wherein the transition metal and ligand are selected to provide the product at room temperature.

*Sub
Cl*

79. The method of claim 21, 41, 53, or 65, wherein the transition metal and ligand are selected to provide the product when X is chloride.

80. The method of claim 21, 41, 53, or 65, wherein the transition metal and ligand are selected to provide the product utilizing less than 0.01 mol% of the catalyst relative to the 5 limiting reagent.

81. The method of claim 21, 41, 53, or 65, wherein the transition metal and ligand are selected to provide the product utilizing less than 0.0001 mol% of the catalyst relative to the limiting reagent.

82. The method of claim 21, 41, 53, or 65, wherein the transition metal and ligand are 10 selected to consume the limiting reagent in less than 48 hours.

*Sub
Cl*

83. The method of claim 21, 41, 53, or 65, wherein the transition metal and ligand are selected to consume the limiting reagent in less than 24 hours.

84. The method of claim 21, 41, 53, or 65, wherein the transition metal and ligand are selected to consume the limiting reagent in less than 12 hours.

15 85. The method of claim 21, 41, 53, or 65, wherein the transition metal and ligand are selected to give the product in a yield of greater than 50% in less than 48 hours.

86. The method of claim 21, 41, 53, or 65, wherein the transition metal and ligand are selected to give the product in a yield of greater than 50% in less than 24 hours.

87. The method of claim 21, 41, 53, or 65, wherein the transition metal and ligand are 20 selected to give the product in a yield of greater than 50% in less than 12 hours.